



Lord, OT., Walter, MJ., Dasgupta, R., Walker, D., & Clark, SM. (2009). Melting in the Fe–C system to 70 GPa. *Earth and Planetary Science Letters*, 284(1-2), 157 - 167. <https://doi.org/10.1016/j.epsl.2009.04.017>

Peer reviewed version

Link to published version (if available):
[10.1016/j.epsl.2009.04.017](https://doi.org/10.1016/j.epsl.2009.04.017)

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Melting in the Fe-C system to 70 GPa

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Total number of words in Main text: 6560

Abstract: 349

Number of figures: 10

Number of Supplementary figures: 3

Number of Supplementary tables: 1

References: 59

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1 **Abstract**

2 We determined high pressure melting curves for Fe_3C , Fe_7C_3 and the Fe– Fe_3C eutectic using laser-
3 heated diamond anvil cell techniques. The principle criterion for melting is the observation of
4 plateaus in the temperature vs. laser power function, which is an expected behavior at isobaric
5 invariant points (e.g. congruent, eutectic, or peritectic melting) as increased power provides the
6 latent heat of melting. We verified this technique by reproducing the melting curves of well-studied
7 congruently melting compounds at high pressure (Fe, Pt, FeS, Pb), and by comparison with melting
8 determinations made using thermocouple-based large volume press techniques. The incongruent
9 melting curve of Fe_3C measured to 70 GPa has an apparent change in slope at ~ 8 GPa, which we
10 attribute to stabilization of Fe_7C_3 at the solidus and the creation of a P - T invariant point. We
11 observe that Fe_7C_3 melts at higher temperatures than Fe_3C between 14 and 52 GPa and has a steep
12 P - T slope, and on this basis predict an expanding field of Fe_7C_3 + liquid with pressure. The Fe- Fe_3C
13 eutectic melting curve measured to 70 GPa agrees closely with multi-anvil data and thermodynamic
14 calculations. We also measured the eutectic composition as a function of pressure using an in situ
15 X-radiographic imaging technique, and find a rapid drop in carbon in the eutectic composition
16 above about 20 GPa, generally consistent with previous thermodynamic calculations, and predict
17 that the eutectic lies close to pure iron by ~ 50 GPa. We use these observations to extrapolate phase
18 relations to core-relevant pressures. Convergence of the Fe_3C and Fe- Fe_3C eutectic melting curves
19 indicate that Fe_3C is replaced at the solidus by Fe_7C_3 at ~ 120 GPa, forming another P - T invariant
20 point and a new eutectic between Fe and Fe_7C_3 . Thus, Fe_3C is unlikely to be an important
21 crystallizing phase at core conditions, whereas Fe_7C_3 could become an important crystallizing
22 phase.

23

24 *Keywords:* Carbon; core; iron carbide; light element

25

26

27 **1. Introduction**

28 The composition of Earth's core has long been subject to controversy. Measurements of the
29 room temperature equation of state of pure iron and iron-nickel alloys to two megabars and beyond
30 (Dewaele et al., 2006; Mao et al., 1990) have consistently yielded higher densities than predicted
31 from geophysical models (Birch, 1952; 1964). Although thermal expansion at the temperatures
32 likely to be relevant to the core partially mitigates the problem (Alfè et al., 2004; Boehler, 1993;
33 Luo and Ahrens, 2004; Ma et al., 2004; Shen et al., 1998), recent determinations of the thermal
34 equation of state of iron at high pressures (Dubrovinsky et al., 2000), extrapolated to core
35 temperatures, still leaves the core insufficiently dense. Recent estimates of the core density deficit
36 range from 3-10% for the outer core (Anderson and Isaak, 2002; Shanker et al., 2004) and 2.5-9%
37 for the inner core (Dewaele et al., 2006; Dubrovinsky et al., 2000), although the magnitude of the
38 deficit depends strongly on the chosen thermal profile.

39 Several possible contenders have been proposed for the alloying elements, including
40 hydrogen, carbon, oxygen, silicon and sulfur (Poirier, 1994), with the popularity of each waxing
41 and waning, and some mixture seems most likely (e.g. Alfè et al., 2002; Badro et al., 2007;
42 McDonough, 2003). Constraining the composition of the core is critical if we are to better
43 understand its thermal structure and crystallization history, dynamo action, energy balance,
44 postulated interaction with the mantle, and the partitioning of siderophile elements (Buffett et al.,
45 2000; Chabot et al., 2006; Jana and Walker, 1997; Lister and Buffett, 1998; Walker, 2005).
46 Although a great deal has been achieved in this area (e.g.: Li & Fei, 2003), much remains to be
47 determined about the relevant iron-light element phase diagrams at pressures relevant to the core's
48 formation and its present state.

49 Carbon is the fourth most abundant element in the solar system, with the CI chondrites
50 containing 3.5 wt% C (Lodders, 2003). The potential importance of carbon in the cores of the
51 terrestrial planets is suggested by the presence of both graphite and cohenite (Fe,Ni)₃C in iron
52 meteorites (e.g.: Goodrich, 1992). It is estimated that the bulk silicate Earth has about 120 ppm

53 (McDonough and Sun, 1995) to 400 ppm (Javoy, 1997) carbon, which is a small amount when
54 compared to the chondrites. Whether this mismatch reflects a low overall abundance in Earth due to
55 volatile loss during accretion or to sequestration into the core during core formation is an open
56 question. As a result of these difficulties, estimates of the Earth's carbon content are speculative and
57 diverse, ranging from as low as 0.2 wt% (Dasgupta and Walker, 2008; McDonough, 2003) to 4
58 wt% (Hillgren et al., 2000). Carbon is thus a potential and interesting candidate for at least part of
59 the light element budget of the core, which makes understanding the Fe-C phase diagram at high
60 pressures a priority.

61 The iron-rich portion of the Fe-C binary system has been studied extensively at 1 atm and
62 modest pressures due to its importance in metallurgy (e.g. Chipman, 1972; Strong and Chrenko,
63 1971), as shown in Fig. 1. At 1 atm (Fig. 1a) there is a eutectic, possibly metastable, between iron
64 and graphite at 1420 K and 4.3 wt% carbon. The compound, Fe_3C (cementite), melts incongruently
65 to liquid + graphite at about the eutectic temperature. At higher pressure (e.g. 5.7 GPa; Fig. 1b),
66 Fe_3C melts in a peritectic reaction to form liquid + diamond, and a eutectic exists between Fe and
67 Fe_3C . At higher pressures still another important compound, Fe_7C_3 , stabilizes and is known to melt
68 incongruently to liquid + diamond at 9 GPa (Shterenberg et al., 1975; Tsuzuki et al., 1984).

69 Wood (1993) calculated phase relations up to 136 GPa in the Fe-C system on the basis of a
70 thermodynamic model, and predicted that pressure would cause a decrease in the carbon content of
71 the eutectic between Fe and Fe_3C , with the carbon content becoming negligible at core pressures.
72 This was predicted to occur because of a rapid increase in the melting point of Fe_3C and a
73 consequent expansion of the Fe_3C + liquid field. Wood (1993) also predicted that Fe_3C melts
74 incongruently at low pressures to liquid + graphite, but that melting becomes congruent by 15 GPa.
75 Thus, for a planetary core in which the entire light element budget consists of carbon, the inner core
76 would consist of pure Fe_3C , with a residual outer core liquid that would have decreasing carbon
77 content as crystallization progressed. However, neutron diffraction measurements (Wood et al.,
78 2004) and ab initio calculations (Vocadlo et al., 2002) have established that the effect of the

ferromagnetic to paramagnetic transition in Fe_3C (Häglund et al., 1991) changes its thermoelastic parameters relative to those used by Wood (1993). These changes are expected to substantially reduce the high-pressure stability field of Fe_3C , calling the predicted phase relations into question. Further, the presence of Fe_7C_3 , which becomes stable above 6 GPa (Shterenberg, 1975; Tsuzuki et al., 1984; Nakajima et al., in press), may also affect the phase diagram in ways not fully captured by the earlier modeling of Wood (1993).

Here we investigate melting phase relations at high pressures in the system Fe-C to further test the proposed phase relations of Wood (1993), corroborate more recent large volume press studies, and extend our knowledge of the Fe-C system to pressures more relevant to the core. Specifically, we have measured the first melting curves of Fe_3C , Fe_7C_3 and the Fe- Fe_3C eutectic to ~70 GPa using the laser-heated diamond anvil cell (LHDAC), and determined the eutectic composition in situ to 44 GPa using a novel X-radiographic imaging technique (Walker et al., 2009). We also report piston-cylinder and multi-anvil quench determinations of Fe_3C melting at lower pressures. We use these data to construct phase diagrams for the Fe-C binary at high pressures, and to assess the role of carbon-rich phases during core crystallization in Earth.

2. Experimental Methods

High-pressure melting experiments were made in symmetric diamond anvils cells (DAC) using diamonds with 200–300 μm diameter culets. Samples were loaded into 80–130 μm holes drilled in stainless steel or rhenium gaskets pre-indented to ~50 μm thickness. In conjunction with the DAC experiments, several synthesis and melting experiments were made in piston-cylinder and multi-anvil apparatus at Lamont-Doherty Earth Observatory (LDEO), for which the details of the experimental methods can be found elsewhere (Dasgupta and Walker, 2008).

105 2.1 Fe_3C and Fe_7C_3 Melting Experiments

106 The Fe_3C starting material was synthesized from pure iron wire placed in a graphite capsule
107 and held for 2 days at 2 GPa and 1473 K in a piston cylinder apparatus. The Fe_7C_3 starting material
108 was synthesized at 7 GPa and 1623 K for 7 minutes in a multi-anvil press using the same method as
109 for the Fe_3C . Both syntheses were carried out at LDEO, and phase purity was confirmed for each by
110 XRD and EPMA (Dasgupta and Walker, 2008). Starting materials were ground under ethanol in an
111 agate mortar to produce a fine powder with a grain size of $\sim 3\text{ }\mu\text{m}$, and then compressed into a dense
112 foil with a thickness of $\sim 10\text{--}15\text{ }\mu\text{m}$. Fragments of these foils were used as samples instead of loose
113 powder to minimize sample deformation and thickness variations during compression. Starting
114 materials were placed in an oven at $125\text{ }^\circ\text{C}$ for at least one hour before loading. The carbide foils
115 were loaded into a gasket hole between thermal insulating layers to allow efficient heating of the
116 sample, to minimise temperature gradients, and to act as the pressure medium. We used several
117 kinds of insulators including single-crystal sapphire discs ($125\text{ }\mu\text{m}$ in diameter and $15\text{--}20\text{ }\mu\text{m}$ thick),
118 dense foils of ruby powder ($10\text{--}15\text{ }\mu\text{m}$ thick), sol gel deposited Al_2O_3 , and NaCl. Dubrovinsky et al.
119 (2001) observed the formation of Fe_3Al and an Fe-Al alloy when iron and Al_2O_3 were reacted in the
120 LHDAC above 60 GPa, but we observe no such phases in our experiments in Al_2O_3 at similar
121 conditions, based on synchrotron X-Ray Diffraction data. NaCl is preferred because it has a low
122 shear strength, which promotes quasi-hydrostatic conditions in the sample chamber at high
123 pressures and minimizes the pressure drop on heating caused by stress relaxation, but can only be
124 used at higher pressures (e.g. $> 40\text{ GPa}$) where the NaCl melting curve rises above that of the
125 samples (Boehler et al., 1997). A recent study by Rouquette et al. (2008) indicates that iron heated
126 at 2700 K and 58 GPa in the LHDAC using NaCl insulators reacts to form Fe_3C , suggesting NaCl is
127 not impervious to carbon diffusion. We see similar results in XRD analyses of quenched iron
128 melting experiments using NaCl (but not Al_2O_3), though the amount of Fe_3C produced is very
129 small. However, when different insulators are used over a similar pressure range, we find no
130 resolvable dependence of melting temperatures on the pressure medium.

131 Melting experiments on Fe_3C were also carried out at 2 to 6 GPa using a piston cylinder
132 (PC: 2 ± 0.1 GPa: Dasgupta and Walker, 2008) and a Walker-style multi-anvil apparatus (MA: 5 ± 0.5
133 and 6 ± 0.5 GPa) at LDEO. All the experiments employed 1.5-2.0 mm long pure Fe wire of 1 mm
134 diameter in graphite capsules as starting materials. The piston cylinder experiments used a standard
135 $\frac{1}{2}$ " assembly with BaCO_3 pressure cell, graphite external heater, and crushable MgO spacers. The
136 multi-anvil experiments were conducted using 8 mm truncation edge length WC cubes, castable
137 MgO octahedral assemblies with LaCrO_3 heaters, and MgO spacers. Temperature during both the
138 PC and the MA experiments was monitored using $\text{W}_{97}\text{Re}_3/\text{W}_{75}\text{Re}_{25}$ thermocouples placed against
139 the capsule wall with uncertainties of ± 10 K and ± 15 K respectively. Polished sections of the
140 quenched run products were studied by electron probe microanalysis.

141

142 *2.2 Fe-Fe₃C Eutectic Melting Experiments*

143 Eutectic melting experiments as well as in situ X-Radiographic imaging (XRI) experiments
144 to determine the eutectic composition in the Fe-C system are made by melting at the boundary
145 between spatially resolved ingredients of pure iron metal and Fe_3C (Walker, 2005; Walker et al.,
146 2009). The following procedure is found to achieve a well defined and stable boundary even at high
147 sample compression: (1) Pure hardened iron foil is indented in a DAC to ~ 15 GPa, which yields a
148 metal thickness of ~ 20 μm . (2) The indented metal is then drilled with 50 μm holes, which are
149 loaded with powdered Fe_3C and compressed until the material is sufficiently compacted to remain
150 in place. (3) An ~ 100 μm diameter ‘donut’ consisting of the central plug of Fe_3C and a thin annulus
151 of iron is then cut out using an UV laser. The donut with stuffing is then polished using 1 μm
152 diamond-impregnated Mylar, cleaned under acetone and stored in an oven at 125°C until loading,
153 typically between insulating muffins of sol gel bound Al_2O_3 . The sample is then laser-heated at the
154 boundary until first melting occurs as described in section 2.4.

155

156

157 2.3 Pressure measurement

158 Samples were compressed and pressure monitored using the ruby fluorescence scale as
159 calibrated by Mao et al. (1986). Several ruby grains $\sim 3\text{--}5\text{ }\mu\text{m}$ in diameter were placed within the
160 sample chamber in early experiments, although we eventually opted for a thin layer of sub-micron
161 ruby spread across the chamber in order to measure pressure exactly at the melted spot. Pressure
162 was measured before and after melting. We assume that the post-melting pressure represents a
163 minimum estimate of the pressure at melting, as no correction for thermal pressure has been made
164 due to the uncertainty in its estimation. Samples were heated at subsolidus temperatures for several
165 minutes before melting, which reduces considerably radial pressure gradients that can develop
166 during initial compression. Measured pressure gradients across the sample chamber after melting,
167 were generally less than $\sim 1\text{ GPa}$. Pressure losses of $\sim 5\text{ GPa}$ due to annealing of stresses were
168 observed in experiments using sol-gel Al_2O_3 , compared to $<2\text{ GPa}$ when using NaCl. The use of
169 single-crystal sapphire resulted in a drastic pressure drop on annealing of $\sim 10\text{ GPa}$, and so it was
170 abandoned as a pressure medium.

171 The biggest source of uncertainty in the reported pressures is the thermal pressure. Recent in
172 situ melting experiments by Dewaele et al. (2007) using NaCl as a pressure medium indicate
173 thermal pressures at melting of $<3\text{ GPa}$. However, because Al_2O_3 is much harder than NaCl, the
174 thermal pressure in these experiments is likely to be greater and is a positive function of
175 temperature, regardless of the medium employed. Therefore, while the pressures reported here have
176 analytical uncertainties on the order of $\pm 1\text{--}2\text{ GPa}$ it should be born in mind that these represent
177 minima, underestimating the true pressure by perhaps $3\text{--}5\text{ GPa}$.

178

179 2.4 Laser heating and temperature measurement

180 Samples were heated at pressure in a double-sided heating geometry using either a 50 W
181 Nd:YLF CW infrared laser operating in TEM_{01} mode, or a 100 W Nd:YAG CW multimode laser.
182 This system produced stable heated spots with diameters of $\sim 20\text{--}40\text{ }\mu\text{m}$. The incandescent light

183 emitted from the sample was monitored using CCD cameras for visual observation on both sides.
184 The temperature was raised in the sample by increasing the laser power in small increments
185 (typically < 1 watt).

186 Temperatures were measured spectroradiometrically on one side using standard techniques
187 employed at Bristol as described in detail elsewhere (Walter and Koga, 2004). In brief, a magnified
188 image of the heated spot (20x) is focused onto the entrance slit (40 μm width) of an imaging
189 spectrometer equipped with a 2-D CCD (e.g. 1024 x 256 pixels). We pre-align the system so that
190 the image of the heated spot is centered on the slit. This allows sampling of a ‘one-dimensional’
191 temperature profile across the heated spot with a spatial resolution of $\sim 2 \mu\text{m}^2$ (see Supplemental
192 Figure 1).

193 The precision of spectroradiometric temperature measurement is dependant upon the
194 closeness of the fit of the measured spectrum to the Planck or Wien blackbody function (Heinz and
195 Jeanloz, 1987; Kavner and Panero, 2004; Walter and Koga, 2004). Replicate analyses of the
196 calibration lamp yield maximum instrumental precision in temperature measurement of $\sim 0.1\%$
197 relative (note that temperatures measured using the W lamp as an unknown are not subject to
198 chromatic effects because the lamp is at constant temperature across the field of view).

199 Another potential source of uncertainty in both the precision and accuracy of measured
200 temperatures is the chromatic dispersion introduced by the optical elements in the path to the
201 spectrometer, which can have a large effect on calculated temperatures when a steep temperature
202 gradient is present (Benedetti et al., 2007; Boehler, 2000; Walter and Koga, 2004). However,
203 effective mitigation of chromatic effects can be achieved by placing an f-stop between the objective
204 and focusing lens to sample only the near-paraxial rays that produce very little dispersion, and by
205 choosing a wavelength range appropriate for the lens system (Benedetti et al., 2007; Walter and
206 Koga, 2004). An example of fitted spectra and the resulting temperature profile across a laser-
207 heated spot produced at optimum configuration is shown in Supplemental Figure 1. In our melting

208 experiments the precision in the fits to the Wien or Planck functions is typically in the range of 0.1-
209 0.4%, which indicates that chromatic effects are virtually eliminated.

210 To further assess the accuracy of our system we have measured the melting points of Pt, Nb,
211 Mo, Ta, Re and W at 1 atm. A pure metal filament is resistively heated in an Ar gas chamber.
212 Temperature is increased incrementally using a radiometric power supply, and is measured
213 spectroradiometrically at the hot spot of the filament. When melting occurs, the filament breaks,
214 and we estimate the melting temperature from the power-temperature path. Supplemental Figure 2
215 shows the results of replicate analyses of melting points for these metals. Relative to published
216 melting data our results indicate a systematic overestimation of temperature by about 50 to 200 K
217 for these metals. These differences may be a consequence of metal-specific deviations from
218 wavelength independent emissivity ('greybody' behavior). We do not attempt to assign any formal
219 uncertainty in accuracy to our measurements at this point, but caution that uncorrected deviations
220 from greybody behavior will likely cause an overestimation in temperature of the order tens to a
221 few hundred degrees K.

222

223 *2.5 Melt detection*

224 We rely on discontinuities in the temperature vs. laser power function to detect the onset of
225 melting. During laser heating, when a sample reaches an invariant melting point, for example at a
226 binary eutectic or peritectic, the temperature should plateau at the invariant temperature as the laser
227 power provides the latent heat of melting. That is, increasing laser power serves only to increase the
228 volume of melt rather than raise the temperature of the molten material, at least until a certain melt
229 threshold is reached. We have observed that such melting discontinuities are easily and
230 reproducibly detectible, and several typical examples are shown in Fig. 2. Figure 2a shows a
231 common pathology in which peak temperature increases monotonically with laser current (i.e.
232 power) until a threshold is reached, after which further power causes a temperature plateau with
233 fluctuations often of the order ± 50 K. In this particular case during heating of Fe_3C at 43 GPa, we

234 estimate the melting temperature by averaging over the points within the plateau, yielding 2650 K.
235 The assigned uncertainty is derived to encompass the analytical precision in temperature
236 measurement (usually 3-10 K), the position of the plateau (usually 10-50 K) and the temperature
237 gradient within the heated spot (estimated at 40 K), in this case yielding a total of ± 98 K. Figure 2b
238 shows another example in which a long plateau is reached after an initial temperature perturbation
239 during heating at the junction of Fe-Fe₃C at 70 GPa. In this case we estimate melting at 2630 ± 40
240 K. A final and less common example is shown in Fig. 2c, in which a single, large temperature
241 discontinuity occurs after a very systematic increase in temperature, and based on extrapolation we
242 estimate melting at 2970 ± 55 K. We suggest that such large perturbations are related to the loss of
243 the sample's shear strength upon melting leading to a considerable change in sample absorption (as
244 evidenced by holes in the sample foil after experiments in which this behaviour was observed), but
245 consider this melting criterion less robust as such failure could be related to subsolidus softening.
246 However, we have produced consistent melting points in replicate experiments in which both
247 plateaus and extreme perturbations have been used as melting criteria.

248 As a means of validating our melting criteria we have measured the melting curves of Fe, Pt,
249 FeS and Pb at pressures from 5 to 45 GPa (~ 1900 to 2600 K), and these data are compared to data
250 from previous studies in Figure 3. Our melting curve for pure Fe closely matches the melting curve
251 of Boehler (1993), which was determined in an LHDAC using visual identification of melt motion
252 as a melting criterion. We also have acceptable correspondence with the data of Ringwood and
253 Hibberson (1990) that is based on thermocouple temperature measurement in a large-volume
254 apparatus. Overall our melting data show excellent consistency with previously measured melting
255 curves in all cases (Boehler, 1992; Boehler, 1993; Dewaele et al., 2007; Kavner and Jeanloz, 1998).
256 Further, we show below that where our new data overlaps most observations made in large volume
257 apparatus we find good correspondence.

258

259

260 2.6 Eutectic melt composition by X-radiography

261 Determining the composition of a eutectic melt has thus far only been possible by ex situ
262 analysis of quenched run products. However, due to the potential for exsolution of the light element
263 from the melt during cooling, especially in slower quenching large-volume apparatus, re-integration
264 of the melt composition is at best an uncertain task (O'Neill et al., 1998; Walker, 2005). Variation
265 in quench rate among different-sized pressure cells may also contribute to error in measured
266 melting curves (Walker, 2005). DAC experiments quench orders of magnitude more rapidly than
267 large-volume experiments, but it is not clear whether exsolution can still cause problems in
268 analysis. A compounding problem is the intrinsic difficulty in making accurate electron probe or
269 TEM-EDX measurement of carbon in DAC samples. Clearly, an in situ method is preferable. For
270 example, in the recent work of Seagle et al. (2008) the composition of liquids was bounded by in
271 situ XRD determination of phase disappearance with temperature for particular bulk compositions.
272 Another method for direct determination of liquid composition is to melt at the boundary between
273 spatially resolved components (e.g. Fe and Fe₃C) and simultaneously measure the X-ray
274 transmission through the sample. For a binary system, the transmissivity should be a simple
275 function of density and, therefore, composition for samples of uniform thickness. By linear
276 interpolation between the observed transmissivity of the pure solid end member compositions, the
277 transmissivity of the molten regions can potentially yield the melt composition directly (Walker et
278 al., 2009; Walker, 2005). Walker et al. (2009) tested this method in the system Fe-S where the
279 change in eutectic melt compositions is well documented to ~30 GPa, and found excellent
280 reproducibility of known results.

281 Fe-Fe₃C melting experiments were prepared as described above and were heated at beam-
282 line 12.2.2 of the Advanced Light Source, which utilizes a double-sided heating similar to the
283 Bristol system (Caldwell et al., 2007). Temperature measurement and melt detection was identical
284 to the method described above. In all cases melting occurred within error of the melting curve
285 constructed using the Bristol system. During the experiment the sample was bathed in a wide beam

of high energy X-rays (~18 KeV). Transmitted X-rays were then converted to visible light via a CdWO₄ phosphor, which was focused onto a high-resolution CCD camera. Images were taken before, during and after melting at each laser power increment with simultaneous temperature measurement. After acquisition, cross-sections through the images were taken normal to the boundary at the melting location, and the average transmissivity of solid Fe, solid Fe₃C and melt estimated. These values were then used to calculate the composition of the melt. For a detailed description of this technique, see Walker et al. (2009).

3. Results

3.1 The Fe₃C melting curve

Figure 4a shows our melting data for Fe₃C from both diamond anvil and large-volume press experiments (see Supplementary Table). In the piston-cylinder and multi-anvil experiments at 2, 5 and 6 GPa, melting was bracketed by textural analysis of quenched run products. Below the melting temperature, coarse crystalline Fe₃C was the sole phase present in graphite capsules, and above the melting point Fe₃C crystals coexisted with a quenched Fe-C melt, formed of dendritic iron and interstitial Fe₃C (see also Dasgupta and Walker, 2008). The carbon content of the quenched melt, near the Fe₃C out point was determined by EPMA and is 5.7 wt% at 2 GPa (Dasgupta and Walker, 2008), 5.7±0.1 wt% at 5 GPa, and 5.8±0.2 wt% at 6 GPa, which confirms a peritectic melting behavior of cementite to 6 GPa. Overall, our DAC melting determinations at similarly low pressures compare favorably with experiments in large volume apparatus (Fig 4b insert). The melting data have been fitted using the empirically derived Simon equation,

$$T_m = \left[(P_m / A + 1)^{1/C} \right] \cdot T_0$$

where T_m is the high-pressure melting point, T_0 is the ambient pressure melting point, P_m is the pressure at melting and the coefficients A and C are constants (Simon and Glatzel, 1929). This

equation is employed for convenience of extrapolation only, as it has no definite physical basis and is of doubtful applicability to an incongruently melting substance. A single, anomalously low melting point at 60 GPa has been omitted from the fit. The melting slope rises steeply up to ~10 GPa and then flattens off at higher pressures. The Simon fit smoothes this transition, but the fit in the 10–30 GPa region is imperfect and suggests the possibility of a change in slope. We fitted the data using the Kraut-Kennedy equation (Kraut and Kennedy, 1966), which predicts a linear relationship between the melting temperature and the degree of isothermal compression,

$$T_m = T_0(1 + C\Delta V/V_0)$$

where ΔV is the difference between the zero pressure volume, V_0 , and the volume at the pressure of melting of the crystalline phase. The constant, C , is equivalent to $2\gamma_{TH} - 2/3$ where γ_{TH} is the thermal Grüneisen parameter (Hofmeister & Mao, 2003). As with the Simon equation, we employ this formulation for convenience. The absence of a definite physical basis for this form providing a meaningful proxy for pressure and its doubtful applicability to an incongruently melting compound, renders this convenience in making the point about the kink in slope in Fig. 4 at some sacrifice in theoretical purity. The high pressure volumes were calculated using a third order Birch-Murnaghan equation of state, with the parameters $V_{0,483}$, $K_{0,483}$ and $K'_{0,483}$ taken from the ab initio calculations of Vocadlo et al. (2002) for the high temperature (>483 K) paramagnetic phase of Fe_3C relevant here. The results of this analysis are shown in Fig. 4c, and a break in slope in the region of 10 GPa is evident. This change in the melting slope likely corresponds to the required presence of two invariant points along the Fe_3C melting curve, one corresponding to the assemblage $\text{Fe}_3\text{C} + \text{graphite} + \text{diamond} + \text{liquid}$, and another corresponding to the assemblage $\text{Fe}_3\text{C} + \text{Fe}_7\text{C}_3 + \text{diamond} + \text{liquid}$. We describe these phase relations in more detail in the Discussion section below.

Above 10 GPa, our melting curve for Fe_3C is lower than that predicted by the thermodynamic calculations of Wood (1993), the discrepancy reaching ~900 K by 70 GPa. The

reason for the discrepancy between the calculated and measured melting curves may relate to the magnetic transition in Fe_3C , which is a metallic ferromagnet at 1 atmosphere and 300 K (Tsuzuki et al., 1984) but is paramagnetic above the Curie temperature of 483 K (Häglund et al., 1991). Several studies have determined the pressure of this transition at 300 K: 25 GPa from X-ray Emission Spectroscopy (Lin et al., 2004), 10 GPa from X-ray Circular Dichroism measurements (Duman et al., 2005) and 4.3 – 6.5 GPa from Synchrotron Mössbauer Spectroscopy (Gao et al., 2008). Finally, ab initio calculations predict this transition to occur above 60 GPa at 0 K (Vocadlo et al., 2002). These studies also indicate considerable changes in thermoelastic properties across the transition. For example, the 1 atm neutron diffraction data of Wood et al. (2004) show a distinct rise in the coefficient of thermal expansion above the magnetic transition. At high temperatures and pressures, the relevant phase is the non-magnetic form that has a higher bulk modulus and coefficient of thermal expansion, which would tend to reduce the Fe_3C stability field. This seems the most likely explanation for the substantial mismatch between the calculated melting temperatures of Wood (1993) and the measured values presented here.

3.2 *Fe-Fe₃C eutectic*

Figure 5 shows the Fe-Fe₃C eutectic melting P - T curve as determined using the ‘donut’ technique in the LH-DAC at Bristol and the ALS, fitted using the Simon equation (see Supplemental Table). Data from both laser-heating systems agree closely, and our melting curve is in excellent agreement with the multi-anvil quench data of Fei et al. (2007). At all pressures, the data are slightly below the calculated values of Wood (1993) but within mutual error. Only the low-pressure multi-anvil quench data of Hirayama et al. (1993) are anomalous relative to our melting curve.

An example showing the temperature plateau behavior and demonstrating our ability to produce a eutectic melt at the boundary between Fe and Fe_3C is shown in Fig. 6. Heating across the boundary at subsolidus temperatures produces a bi-modal temperature profile with a high-

364 temperature peak on the Fe_3C side of the boundary, as this material heated preferentially to pure Fe.
365 Increased laser power resulted in an eventual plateau in the peak temperature on the Fe_3C side
366 coincident with an increase in temperature on the Fe side. As power was increased further, the
367 temperature on the Fe side rapidly caught up to that on the Fe_3C side, and a stable plateau formed
368 across the boundary that was maintained upon further heating, which we interpret as the eutectic
369 temperature. This example is also very informative because it was taken during X-radiographic
370 imaging at beamline 12.2.2. The observed eutectic melting behaviour corresponds exactly with the
371 emergence of the ledge shown on Fig. 7b as described below, giving us confidence in both the
372 melting criterion and the interpretation of the ledge as a eutectic melt.

373 We have measured the composition of the eutectic liquid between 10 and 44 GPa using the
374 X-radiographic imaging technique described briefly above and in detail in Walker et al. (2009).
375 Figure 7 shows X-ray transmission cross-sections across the laser-heated spot for experiments at 10,
376 19 and 27 GPa. The first panel shows the precipitous drop in transmissivity across the boundary
377 between the Fe_3C plug and iron annulus of the donut before heating. The second panel shows the
378 formation of ledges of intermediate composition that formed at high temperature, representing the
379 formation of a pool of eutectic liquid between the two components. Axial temperature gradients
380 within the sample, probably on the order of 200 K (Campbell et al., 2007), may result in a non-
381 cylindrical melt pool. This interleaving of melt and solid along the X-ray transmission direction
382 may explain in part why the solid/liquid boundaries in the X-ray transmission cross-sections are not
383 perfectly sharp. Linear interpolation of the transmissivity corresponding to the in situ ledges
384 between the transmissivities of the end members yields compositions for the ledges, which are
385 plotted for all experiments in Figure 8. The data show no statistically measurable change in the
386 eutectic composition until ~ 20 GPa, at which point there is a rapid decrease in the eutectic
387 composition to 37 GPa. An experiment carried out at 44 GPa failed to form a detectible ledge even
388 though the melting point was reached and exceeded, which may indicate that the eutectic
389 composition dropped below the detection limit of the technique (~ 0.6 wt%) as determined using the

390 method described in Walker et al. (2009). Our results are in good agreement with the multi-anvil
391 quench data of Chabot et al. (2008) and Hirayama et al. (1993) to 12 GPa. Preliminary results of Fei
392 et al. (2007) indicate little change or a slight reduction in eutectic C content to 20 GPa. The
393 uncertainties in our results and those of Fei et al. (2007) (Fei, personal communication) are such
394 that data from these two studies overlap.

395 The interpretation of the XRI data assumes that the intermediate ledge represents a eutectic
396 liquid and not an Fe-C alloy produced by diffusion, and that the region of the transmission profile
397 taken to represent pure Fe remains so. It is our contention that these assumptions are valid for three
398 reasons: (1) Profiles across the heated region at sub-solidus temperatures show no change in shape
399 compared to profiles taken at 300 K; (2) The observed ledges form immediately the temperature
400 reaches the eutectic melting curve as determined from separate off-line experiments (described
401 above; see figure 6) and do not evolve slowly with time as would be expected for diffusion; (3) The
402 regions used to determine the end-member compositions to which the liquid is compared are well
403 outside the heated region, and thus should not be subject to diffusion. On this basis, we believe the
404 drop in the carbon content of the eutectic with pressure is real, and not the result of an increasing
405 solubility of carbon in solid iron with pressure. Our confidence in the imaging technique is
406 established by the successful determination of the pressure dependence of the composition of the
407 eutectic in the Fe-S system, in which excellent agreement was found with the literature (Walker et
408 al., 2009).

409 Wood (1993) predicted a rapid drop in eutectic carbon content with pressure, from 4.3 wt%
410 C at 1 atm to 2.2 wt% C at 15 GPa. Extrapolation of that trend led Wood (1993) to predict a
411 negligible carbon content at core relevant pressures. The decrease in eutectic composition we
412 observe is similar to the prediction of Wood, although shifted to somewhat higher pressures. Chabot
413 et al. (2008) [and Hirayama et al. \(1993\)](#) found no evidence for a change in the eutectic carbon
414 content [up to 5 GPa and 12 GPa respectively, consistent with our results](#). Fei et al. (2007) observed

no significant pressure dependence of the eutectic composition in multi-anvil experiments up to 20 GPa, within mutual error of our results.

3.2 Melting of Fe_7C_3

We measured the melting curve of Fe_7C_3 from 14 to 52 GPa (Fig. 5). The melting curve has a relatively steep slope compared to Fe_3C , such that by 50 GPa the melting point is about 500 K higher. In contrast, Wood (1993) predicted the two phases would have similar melting points at core conditions. Shterenberg et al. (1975) show that Fe_7C_3 melts incongruently to form diamond + liquid at 9 GPa and ~1950 K, eclipsing the Fe_3C melting temperature. The phase relations at 10 GPa shown by Nakajima et al. (in press) are consistent with this interpretation. Based on these observations we predict that in P - T space the Fe_7C_3 melting curve emerges from the Fe_3C melting curve at ~8 GPa from a P - T invariant point, as described below. We note, however, that while the temperature range of the Fe_7C_3 + liquid field determined here between 15 and 25 GPa is consistent with that measured using in situ XRD in the multi-anvil experiments of Nakajima et al. (in press), their absolute melting temperatures for both phases are considerably lower than those reported here (Fig. 4a). It is noteworthy that in the experiments of Nakajima et al. (2007) iron was loaded into graphite capsules, with no control on the system bulk composition during the experiment (i.e. the capsule becomes part of the system). This conceivably provides an explanation for why the melting temperatures for Fe_3C of Nakajima et al. (in press) coincide so closely with the eutectic temperatures determined in the this study using the LHDAC and in the multi-anvil study of Fei et al. (2007). As already mentioned, our own piston cylinder and multi-anvil experiments closely corroborate our Fe_3C melting temperatures determined in the LHDAC.

441 4. Discussion

442 4.1 The Fe-C system at high pressure

443 The data presented above are used to construct temperature-composition phase diagrams for
444 the iron-rich portion of the Fe-C system from 5 to 130 GPa, shown in Figure 9. Phase relations for
445 the composition Fe_3C are summarized in a pressure-temperature isopleth in Figure 10.

446 At 5 GPa, Fe_3C melts incongruently to liquid + graphite at a temperature about 270 K above
447 the Fe- Fe_3C eutectic (Fig. 9a). The shape of the liquidus is constrained by the eutectic composition,
448 which is unchanged from its one atmosphere composition at this modest pressure (Chabot et al.,
449 2008), and the measured composition of the peritectic liquid. It is possible that Fe_7C_3 is stable in the
450 subsolidus at this pressure, breaking down to Fe_3C + graphite, as shown schematically. At slightly
451 higher pressure graphite transforms to diamond, as shown in Fig. 1b (Strong and Chrenko, 1971),
452 forming another liquidus invariant point at higher temperature. The intersection of the Gr + liquid to
453 Di + liquid curve with the Fe_3C melting curve forms an invariant point in P - T space where four
454 phases coexist (Fe_3C , Gr, Di, and liquid), and this is denoted as I1 in Fig. 10. Between 5 and 10
455 GPa Fe_7C_3 stabilizes and its melting temperature reaches that of Fe_3C , which corresponds to another
456 invariant point in P - T space (point I2 in Fig. 10; See Supplemental Fig. 3a) where Fe_3C , Fe_7C_3 , Di,
457 and liquid coexist. We estimate the position of invariant point I2 at ~8 GPa. At pressures higher
458 than 8 GPa the Fe_7C_3 melting point exceeds that of Fe_3C , creating a new peritectic reaction where
459 Fe_3C melts to form Fe_7C_3 + liquid (Fig. 9b). We show this peritectic at 10 GPa (Fig. 9b) and place
460 the peritectic composition between Fe_3C and Fe_7C_3 , in accordance with the topology of Shterenberg
461 et al. (1975). We preserve this general topology for Fe_7C_3 melting at higher pressures in the absence
462 of further constraints. Overall, the topologies of phase relations in the pressure region of 5 to 10
463 GPa are drawn to be consistent in form with previous results (Nakajima et al., in press; Shterenberg
464 et al., 1975; Strong and Chrenko, 1971; Tsuzuki et al., 1984).

465 We note that the position of invariant point I2 in Fig. 10 (~8 GPa) corresponds well with the
466 inflection in the Fe_3C melting curve interpreted on the basis of the Kraut-Kennedy fits shown in

467 Fig. 4b. We speculate that this occurs because of the change in phase relations brought about by the
468 emergence of Fe_7C_3 at the solidus, and a subsequent expansion of the Fe_7C_3 + liquid field with
469 pressure as shown at 50 GPa in Fig. 9c. At 50 GPa the Fe_7C_3 melting point is about 500 K above
470 that of Fe_3C , and we show an expansion of the Fe_7C_3 + liquid field and also infer a shift in Fe_3C
471 peritectic melt composition to lower carbon contents. If true, this expansion of the Fe_7C_3 + liquid
472 field necessitates that the change in partial molar volume of carbon in going from Fe_7C_3 to melt is
473 positive. We also show that by 50 GPa the composition of the eutectic between Fe and Fe_3C is at
474 less than 1 wt% carbon, as constrained by in situ measurements.

475 The Fe_3C and Fe– Fe_3C eutectic melting curves apparently converge at about 1.2 Mbar based
476 on extrapolation of the Simon curves. The convergence of the Fe– Fe_3C eutectic with the $\text{Fe}_3\text{C} \rightarrow$
477 Fe_7C_3 + liquid peritectic may occur because the melting point of pure Fe increases at a faster rate
478 than does Fe_3C , eventually resulting in the breakdown of Fe_3C to Fe + Fe_7C_3 in the subsolidus. In
479 P - T space this reflects another invariant point where the subsolidus reaction intersects the Fe_3C
480 melting curve at which four phases coexist (Fe, Fe_3C , Fe_7C_3 and liquid), shown as I3 in Fig. 10 (See
481 supplemental Fig. 3b). At pressures above the invariant point a new eutectic would form between
482 Fe and Fe_7C_3 , as shown in Fig. 9d. The composition of the eutectic is impossible to predict reliably
483 but could be richer in carbon than the carbon-poor Fe– Fe_3C eutectic it replaces, with important
484 implications for crystallization of Earth's inner core.

485

486 4.2 Constraints on Earth's Core

487 Although the Earth's metallic core is unlikely to be a binary Fe-C alloy, binary phase
488 relations can be instructive as to the nature of phases that might have crystallized in the solid inner
489 core, as well as to the relative concentration of carbon in the liquid outer core. For example, Wood
490 (1993) predicted that Fe_3C would melt congruently at 136 GPa, and that the Fe– Fe_3C eutectic
491 composition would be nearly pure Fe. On this basis Wood suggested that the inner core might have
492 crystallized an Fe_3C phase, resulting in an outer core that would become carbon depleted as the

493 inner core crystallized, and predicted an inner core density that matches closely constraints from
494 seismology. Vocadlo et al. (2002), however, have convincingly showed on the basis of new elastic
495 parameters that nonmagnetic Fe_3C would have too low a density to match the inner core. Further,
496 Fiquet et al. (2009) have measured V_p in Fe_3C to 83 GPa and found it to be too high to match the
497 inner core. Indeed the authors estimate that the inner core can contain only ~ 1 wt % carbon to satisfy
498 both the density and compressional wave velocity predicted by PREM. Using a similar technique,
499 Gao et al. (2008) determined both V_s and V_p up to 50 GPa, and found both to be larger than PREM
500 after extrapolation to core conditions, ruling out Fe_3C as a sole inner core phase, though the authors
501 suggest some lesser amount of carbon as an excellent candidate for reconciling the sound velocity
502 and density of Fe-Ni alloys with the measured values in the inner core.

503 Similar to the model of Wood (1993), we also find that the Fe- Fe_3C eutectic moves to nearly
504 pure Fe at high pressures. However, Wood has a steep P - T slope for the Fe_3C melting curve, which
505 results in congruent melting of Fe_3C at core pressures, effectively eliminating a role for Fe_7C_3 . In
506 contrast, our phase relations, as well as those of Shterenberg et al. (1975) and Nakajima et al. (in
507 press), suggest an important role for Fe_7C_3 in the Fe-rich region of the phase diagram at high
508 pressures. Our results indicate that the melting point of Fe_7C_3 rapidly diverges from Fe_3C at high
509 pressure, and that the Fe_3C and eutectic melting curves converge (Fig. 10). These features conspire
510 to eliminate Fe_3C at the solidus, with replacement by Fe_7C_3 (Fig. 9d). Thus, the important point for
511 understanding the carbon partitioning between Earth's inner and outer core is the carbon content of
512 the eutectic formed between Fe and Fe_7C_3 , as this together with the bulk core carbon content will
513 control the nature of the crystallizing phase in Earth's core.

514 The carbon content of Earth during core formation is poorly constrained, but likely is in the
515 range of 0.2 to 4 wt.%. If the predicted eutectic between Fe and Fe_7C_3 were close to pure iron, then
516 we would expect that for much of the predicted range of core carbon contents the inner core would
517 crystallize an Fe_7C_3 phase (Nakajima et al., in press). Little is known about the thermoelasticity of
518 this phase at core conditions, but we can predict that given its higher carbon content Fe_7C_3 might

519 provide a poor match for Earth's inner core, at least as a sole crystallizing phase. Conversely, if the
520 Fe-Fe₇C₃ eutectic is at moderate carbon contents as drawn in Fig. 9d, then the core could crystallize
521 a carbon-poor Fe phase, with the carbon content in the outer core increasing as crystallization
522 proceeds. In this case effectively all the core's carbon budget would reside in the liquid outer core.

523

524 **5. Conclusions**

525 We have measured the melting curves of Fe₃C, Fe₇C₃, and the Fe-Fe₃C eutectic up to ~70
526 GPa. We find a change in slope of the Fe₃C melting curve at ~8 GPa that corresponds with the
527 emergence of Fe₇C₃ at the solidus and the creation of a *P-T* invariant point. At pressures below the
528 invariant point our Fe₃C melting curve is consistent with that predicted from thermodynamic
529 calculations (Wood, 1993), but at pressures higher than the invariant point our melting curve
530 flattens and by 70 GPa is ~1000 K below that of Wood (1993). In contrast to Fe₃C, we find a steep
531 *P-T* slope for the Fe₇C₃ melting curve, and on this basis predict an expanding field of Fe₇C₃ + liquid
532 with pressure. Our measurements of the Fe-Fe₃C eutectic temperature are in close agreement with
533 the multi-anvil data of Fei et al. (2007) and to the thermodynamic calculations of Wood (1993). The
534 eutectic composition, measured in situ using a novel X-radiographic imaging technique, drops
535 rapidly with pressure, generally consistent with the prediction of Wood (1993), and has a
536 composition with less than 1% carbon by ~50 GPa. The resulting phase relations, though requiring
537 significant extrapolation to core pressures, suggest that Fe₃C will be replaced at the solidus by
538 Fe₇C₃ at ~120 GPa, thereby forming a new eutectic between Fe and Fe₇C₃. Until phase relations are
539 determined at megabar pressures and beyond we can only speculate regarding the nature of a
540 carbon-bearing phase that might be crystallizing in the inner core. For Fe₇C₃ to crystallize in the
541 inner core the proposed eutectic between Fe and Fe₇C₃ would have to be at a composition poorer in
542 carbon than the bulk core carbon content. We speculate that the opposite case is also possible, and
543 that the core carbon content is on the carbon-poor side of the eutectic such that carbon is expelled
544 nearly wholesale to the liquid outer core.

545

546 **Acknowledgements**

547 We thank J. Knight at ALS for technical support during the imaging experiments. RD
548 acknowledges support of LDEO post-doctoral fellowship. OTL acknowledges support of a NERC
549 PhD studentship. This work supported by NERC grant NE/C511548/1 to MJW and by NSF grants
550 to DW. The Advanced Light Source is supported by the Director, Office of Science, Office of
551 Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-
552 05CH11231. This research was partially supported by COMPRES, the Consortium for Materials
553 Properties Research in Earth Sciences under NSF Cooperative Agreement EAR 06-49658.

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709

710 **Figure Captions**

711 Fig. 1. The iron rich portion of the Fe-C phase diagram at 1 atmosphere after Chipman (1972) and
712 at 5.7 GPa after Strong and Chrenko (1971). The dashed line in the 1 atmosphere diagram indicates
713 that the liquid + Fe₃C field is metastable. The arrow at 8.41 wt% C indicates the location of Fe₇C₃,
714 which does not become stable until higher pressure. L = liquid; Gr = graphite; Di = diamond.

715

716 Fig. 2. Typical power vs. temperature functions from Fe₃C melting experiments. (a-b) In these two
717 cases the temperature plateaus with increasing power, and the melting point is taken as the average
718 of the points within the plateau, while the error bars represent their standard deviation. (c) In this
719 less common example, the temperature drops suddenly on melting. Here, a linear fit to the power
720 vs. temperature function is extrapolated to the next acquisition. The melting temperature is taken as
721 the center point between this and the previous measured temperature, with the uncertainty
722 encompassing the two points. Within each experiment, care was taken to ensure the time between
723 acquisitions remained constant, and is on the order 5-20 seconds in most experiments. Uncertainty
724 due to the precision of temperature measurement is smaller than the symbol size in all cases. Each
725 acquisition number (x-axis) represents an increase in laser current; the increments are equal, and so
726 the axis is simply a proxy for power, which was not directly measured.

727

728 Fig. 3. Melting data for FeS (open diamonds), Fe (open squares), Pt (open circles) and Pb (open
729 triangles) using our laser DAC, temperature measurement techniques and melting criteria. Our data
730 is compared to literature melting data as a test of consistency. Solid line, DAC melting data for FeS
731 from Boehler (1992); filled squares, multi anvil melting point of iron from Ringwood and
732 Hibberson (1990); short dashed line, DAC melting data for Fe from Boehler (1993); dotted line,
733 DAC melting data for Pt from Kavner and Jeanloz, (1998) and long dashed line, DAC melting data
734 for Pb from Dewaele et al. (2007).

735

Fig. 4. The Fe₃C melting curve. (a) Melting temperatures from DAC laser heating experiments (open circles, Bristol; closed circles, ALS) and melting brackets from piston cylinder and multi anvil quench experiments (closed triangles) are shown. The solid line is a fit to the data, excluding the anomalously low point at 60 GPa, using the empirically derived Simon equation, and the dotted line indicates the Fe₃C melting curve from the thermodynamic calculations of Wood (1993). The long dashed line represents the multi-anvil melting data of Nakajima et al. (in press). The inset (b) shows the low-pressure region of the melting curve from (a) expanded for clarity, illustrating the close agreement between DAC and large volume press melting data. The 2 GPa piston cylinder data were previously reported in Dasgupta and Walker (2008), and along with the multi-anvil data at 5 and 6 GPa have uncertainties in temperature and pressure much smaller than the symbol size. (c) Melting data plotted against isothermal compression of the paramagnetic phase of Fe₃C. The compression has been calculated using a 3rd order Birch-Murnaghan Equation of State and the calculated parameters $V_{0,483}$, $K_{0,483}$ and $K'_{0,483}$ taken from Vocadlo et al. (2002). The solid lines are fits to the data using the Kraut-Kennedy equation (Kraut and Kennedy, 1966). The low pressure curve was fitted to the black circles, the high pressure curve to the white ones, while the grey symbols were included in both fits. Note the inflexion around a compression value of 0.03. We interpret this as possibly representing a change in the peritectic melting reaction from Fe₃C → liquid + diamond to Fe₃C → liquid + Fe₇C₃, which also produces an invariant point in P-T space (~8 GPa). The grey region represents an estimate of uncertainty on the position of this invariant point.

Fig. 5. Melting curves of Fe₇C₃ and the Fe-Fe₃C eutectic. The eutectic melting curve is determined from LH-DAC experiments using the ‘donut’ technique for melting at a boundary between spatially resolved ingredients (open circles, Bristol; closed circles, ALS). The data are fitted to a Simon equation (solid line). The dotted line is the calculated eutectic curve of Wood (1993), the dashed line is a linear fit to the multi anvil quench data of Fei et al. (2007), and the dash-dot line a linear fit

762 to the data of Hirayama et al. (1993). The solid squares show melting determinations for Fe_7C_3 ,
763 which have been fitted with a Simon equation.

764

765 Fig. 6. Sequence of temperature profiles acquired during heating at the boundary between Fe and
766 Fe_3C , with an approximate boundary denoted by the dashed line. At first the temperature in the
767 Fe_3C is higher than the iron, as it more readily absorbs the laser radiation (lightest grey line). As
768 laser power is increased the temperature rises and then plateaus around 1900 K, indicating melting
769 has occurred. Simultaneously, the temperature of the Fe rises, until it equalizes with the Fe_3C
770 temperature, suggesting the formation of a homogenous melt pool at the boundary. These data were
771 acquired simultaneously with X-radiographic images of the boundary region, which show the
772 formation of the melt (see figure 7b).

773

774 Fig. 7. Examples of cross sections from X-radiographic images of Fe- Fe_3C ‘donuts’ used to
775 determine eutectic composition. The left hand panel in each case shows the initial boundary at 300
776 K before laser heating. The X-ray transmissivity is higher on the left (the Fe_3C) than the right (the
777 Fe) (a) 10 GPa: In the right hand panel, during in situ laser heating, a small but well-defined ledge
778 has formed, representing the presence of a eutectic melt. (b) 19 GPa: The ledge in the example
779 formed at 1875 K, simultaneously with a plateau in the measured temperature (see figure 6). The
780 contrast between the iron and Fe_3C is larger in this example than the others, because the exposure
781 time was longer. (c) 27 GPa: In this case, the ledge formed at 2160 K. For the sake of clarity, in
782 each panel the y-axis scaling has been altered so that the positions of the lines representing the
783 transmissivity of Fe and Fe_3C line up across the diagram.

784

785 Fig. 8. The pressure dependence of the Fe- Fe_3C eutectic as determined by in situ LH-DAC X-
786 radiographic imaging. Error bars represent the estimated uncertainty in finding the plateau position,
787 except where this is smaller than the uncertainty due to the detection limit. The filled diamond

788 represents an experiment at 44 GPa which yielded no ledge during heating, suggesting the solubility
789 may have dropped to less than the detection limit; the error bar encompasses the noise within the Fe
790 baseline where a plateau might be hidden. The open circles and open square represent the multi-
791 anvil quench data of Hirayama et al. (1993) and Chabot et al. (2008), respectively. The filled square
792 indicates the 1 atmosphere eutectic from Chipman (1972).

793

794 Fig. 9. The Fe-rich portion of the Fe-C phase diagram at 5, 10, 50 and 130 GPa, inferred from
795 measurements of the melting curves of Fe_3C , Fe_7C_3 and the Fe- Fe_3C eutectic, as well as eutectic
796 compositions determined from X-radiographic imaging experiments. The melting curve of iron is
797 from Shen et al. (1998; 2004). L, liquid; Gr, graphite; Di, diamond; Values in italics represent
798 melting temperatures and those in bold represent compositions. Dashed lines are used where the
799 phase relations are inferred.

800

801 Fig. 10. Pressure-temperature phase diagram for Fe_3C (the Fe- Fe_3C melting curve is also shown as
802 grey line). Construction and symbols as in Figure 9. Filled circles represent P - T invariant points.
803 Point I1 represents the intersection of the graphite + liquid to diamond + liquid curve with the Fe_3C
804 melting curve. Point I2 represents a change in the Fe_3C peritectic reaction products from diamond +
805 liquid below ~ 8 GPa to Fe_7C_3 + liquid at higher pressures. Point I3 represents the predicted
806 intersection between the Fe_3C and Fe- Fe_3C melting curves, at which point a new P - T invariant
807 forms that also corresponds to the elimination of Fe_3C at the solidus (also shown as a dashed line is
808 a subsolidus univariant reaction where Fe_3C breaks down to $\text{Fe} + \text{Fe}_7\text{C}_3$). At pressures higher than
809 point I3, Fe_3C composition melts at a new eutectic between Fe and Fe_7C_3 . The graphite to diamond
810 transition is after Bundy et al. (1994).

811

812 Supplemental Fig. 1. A typical spectroradiometric temperature measurement for Fe_7C_3 at 52 GPa in
813 the laser heated diamond cell. (a) Normalised intensity (J) vs. normalized wavelength (ω), where

814 $c_1 = 2\hbar c^2$ and $c_2 = \hbar c / k$ (c , speed of light; \hbar , Planck's constant; k , Boltzman's constant). Each curve
815 represents the system response to the incandescent light emitted from a region along a transect
816 across the laser heated spot, fitted using the Wien approximation. (b) A fit to each wavelength-
817 intensity spectrum yields a temperature, which is used to produce a cross-section. The fitting error
818 averaged over all points in the profile is 5.6 K. For a melting determination, the peak temperature is
819 used, which in this case is 3280 K. Fitting the data using the Wien approximation (solid line) and
820 Planck function (dashed line) yield temperatures which deviate by only ~20 K at ~3300 K.

821

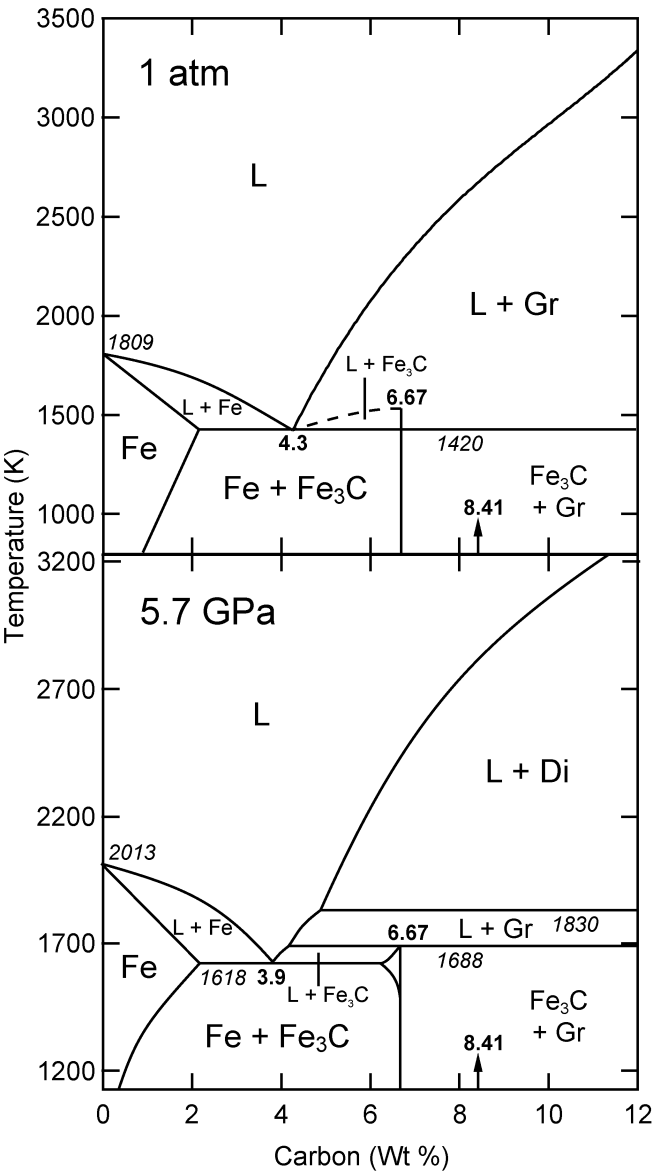
822 Supplemental Fig. 2. Determination of metal melting points at 1 atm using resistance heating and
823 spectroradiometry. The filled circles represent replicate analyses except for Nb and Ta, which
824 represent a single analysis. The solid line indicates the expected 1:1 correspondence between
825 known and measured melting points. In all cases the symbol size is larger than the error bars. The
826 markers on the right hand y-axis indicate the melting points as derived from the literature (Weast et
827 al., 1985).

828

829 Supplemental Fig. 3. The phase reaction topology around invariant points I2 and I3 in Figure 10.
830 Di, diamond; L, liquid. Solid lines are univariant equilibria and dashed lines are their metastable
831 extensions. The phase in parentheses labeling each univariant curve is the 'phase out' in the given
832 reaction.

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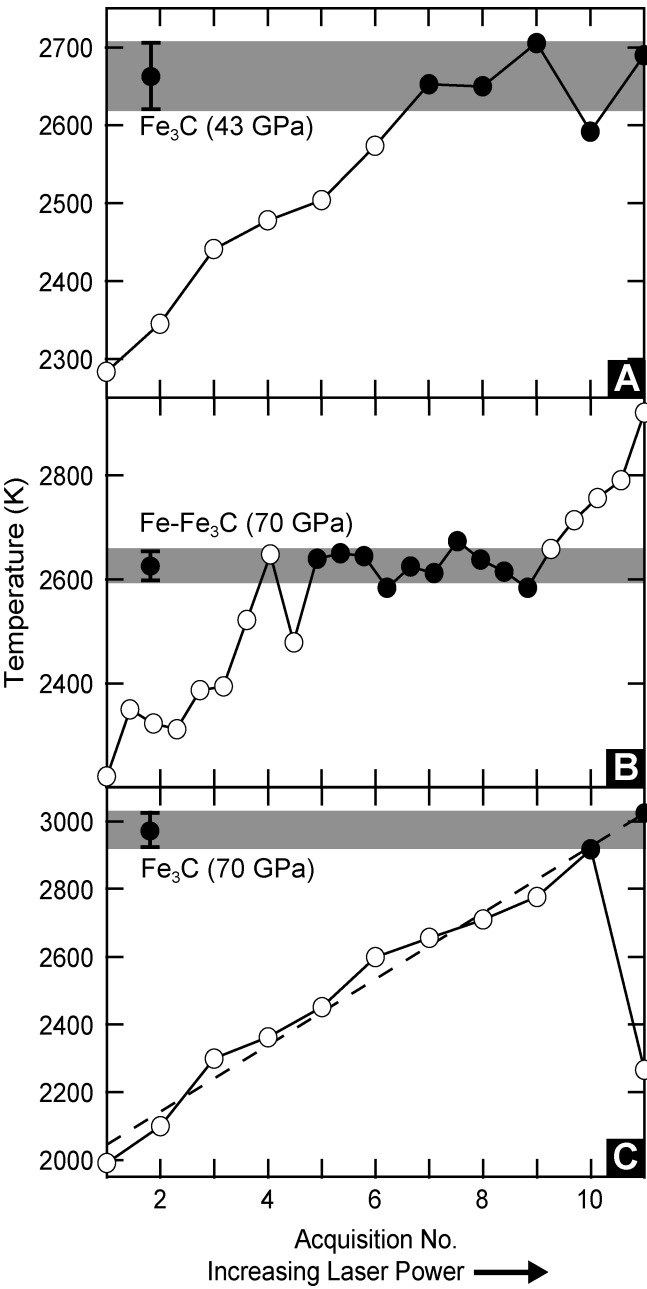
834 **Figure 1**



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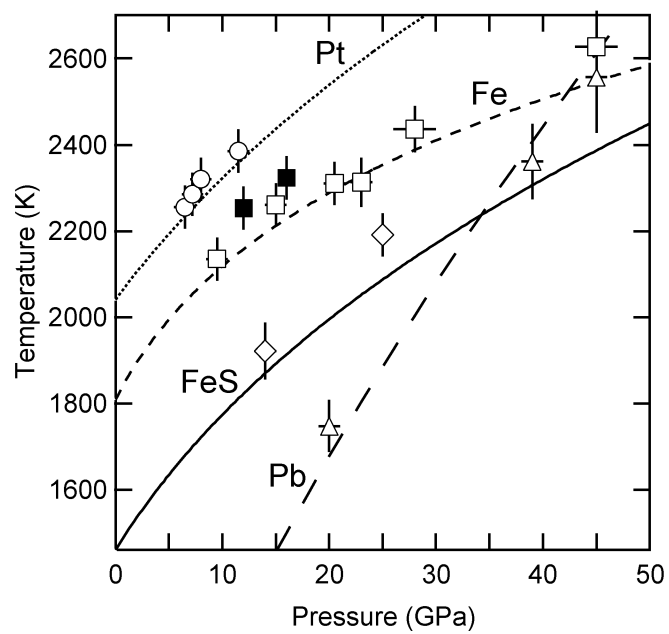
837 **Figure 2**



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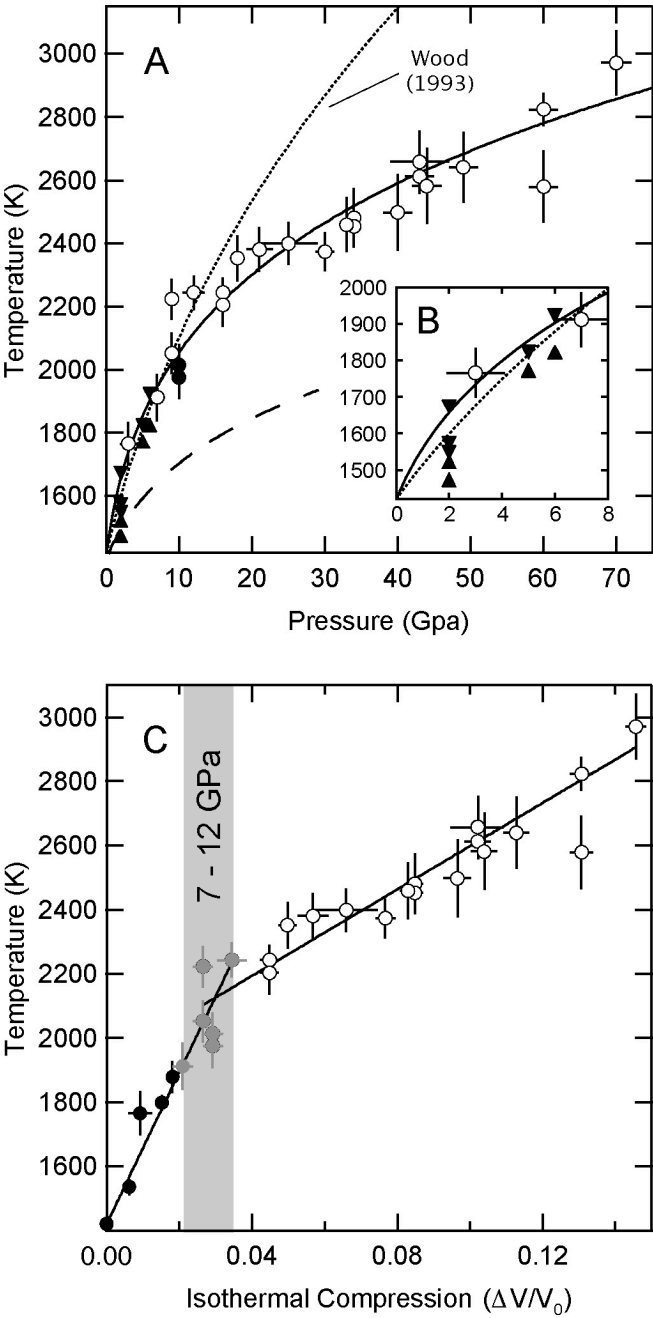
840 **Figure 3**



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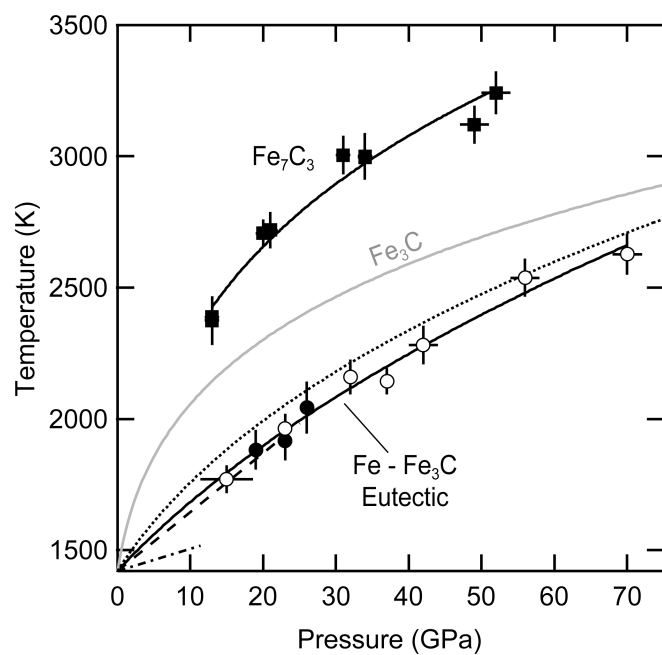
843 **Figure 4**



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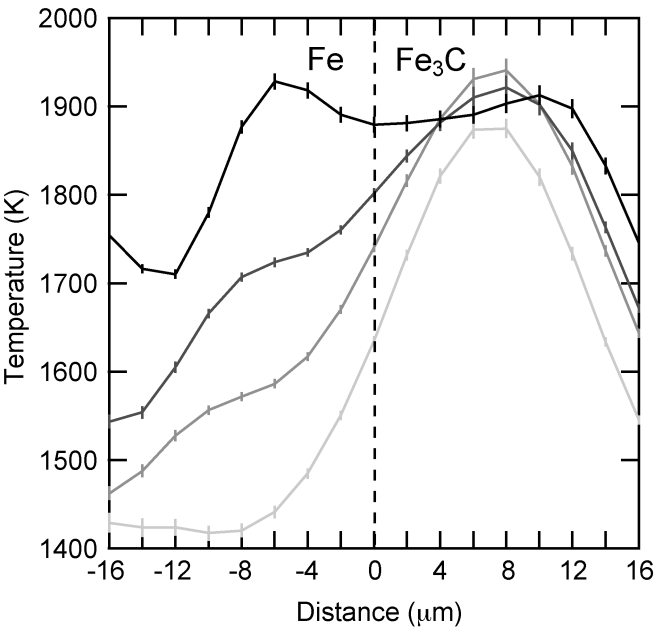
846 **Figure 5**



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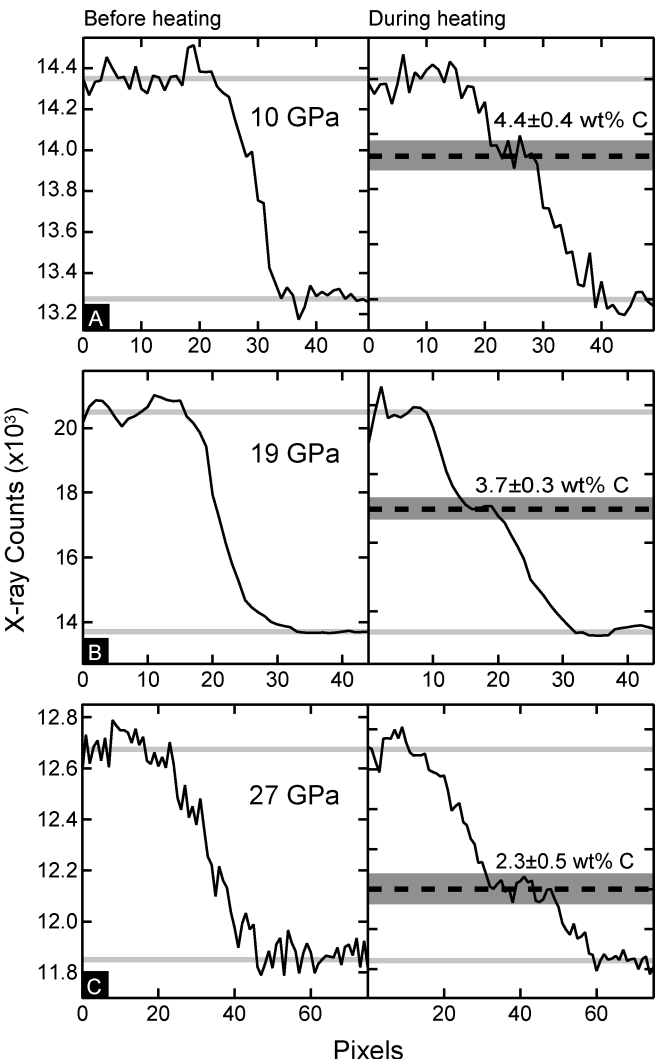
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849 **Figure 6**



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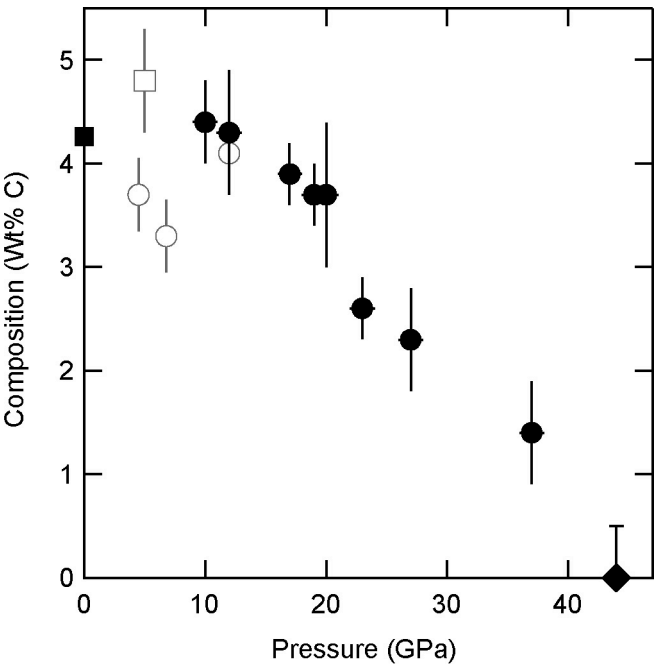
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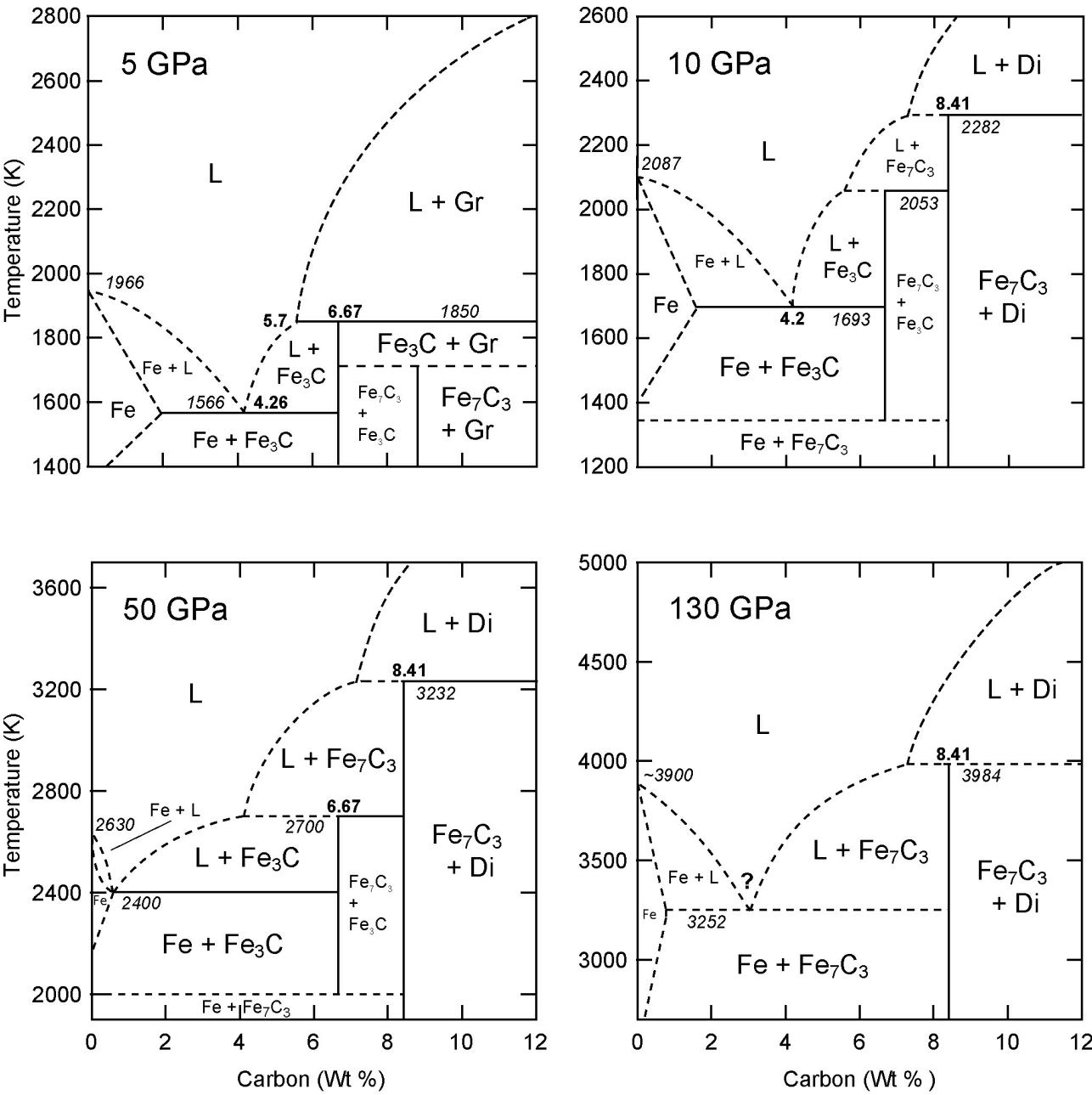
855 **Figure 8**



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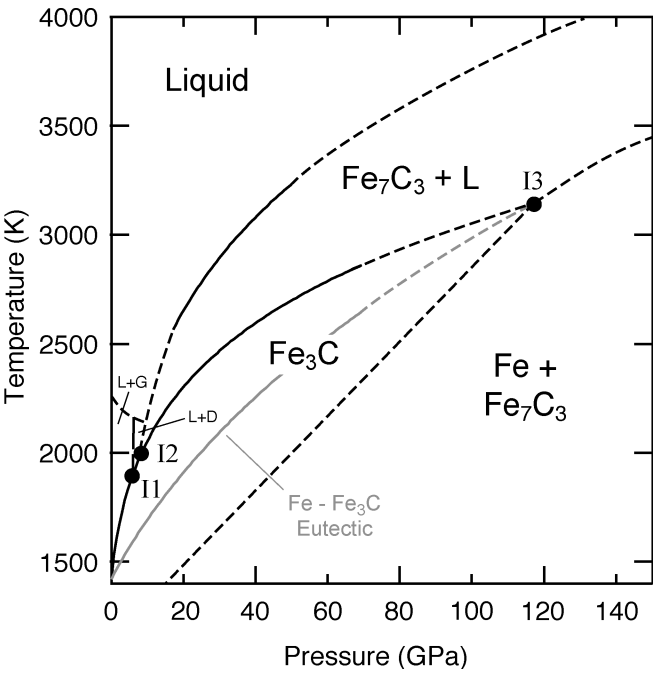
858 **Figure 9**



859

860

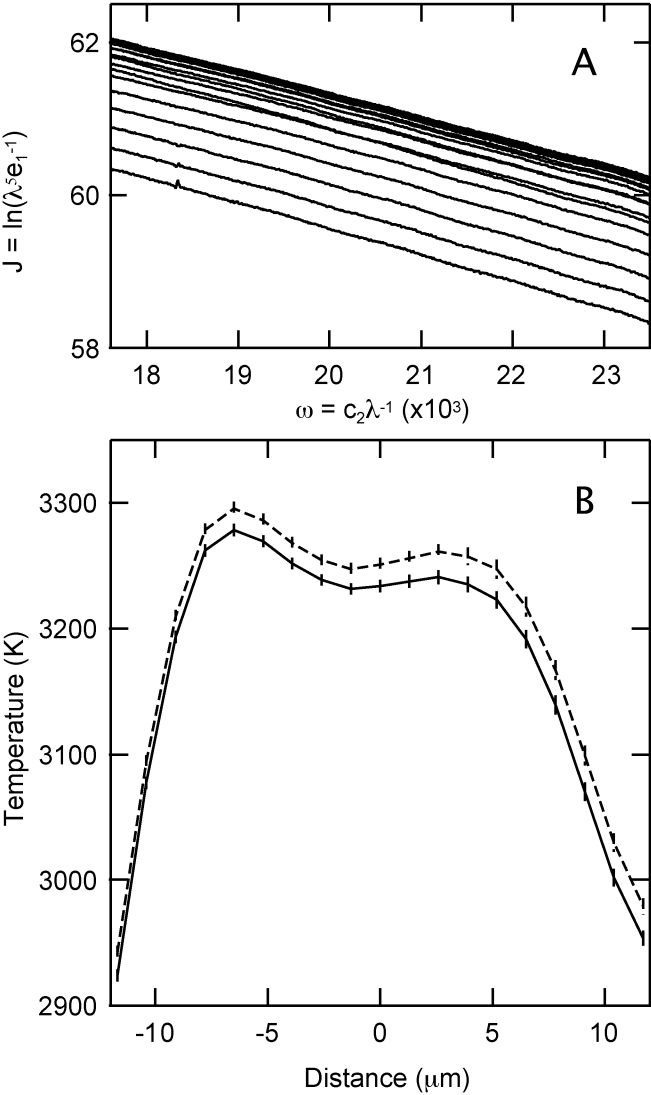
861 **Figure 10**



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863

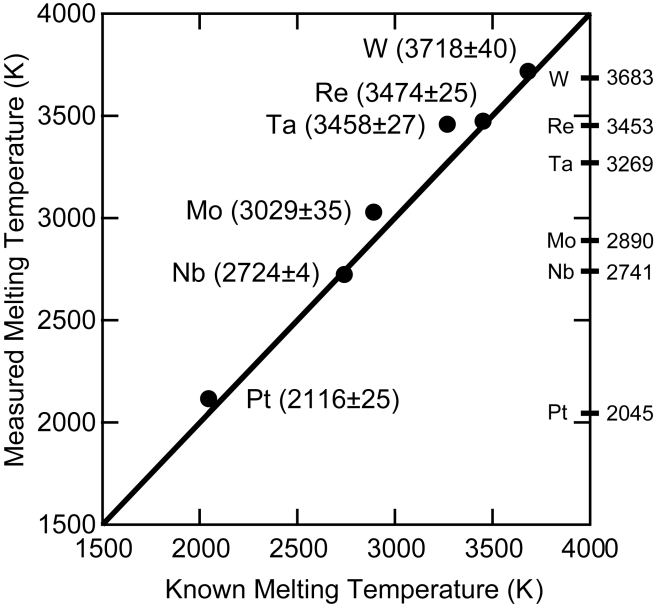
864 **Supplemental Figure 1**



865

866

867 **Supplemental Figure 2**

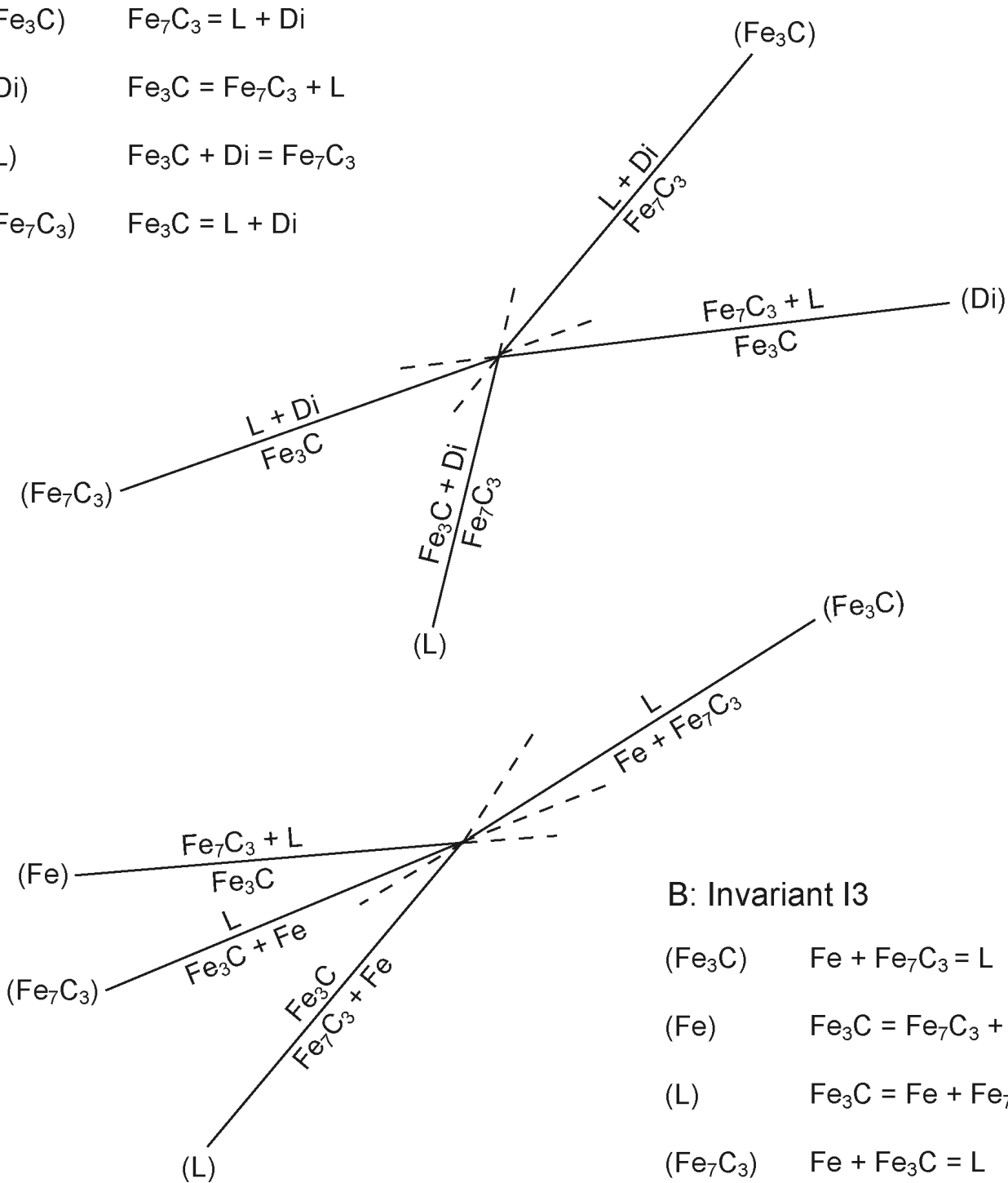


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869

A: Invariant I2

- (Fe₃C) Fe₇C₃ = L + Di
- (Di) Fe₃C = Fe₇C₃ + L
- (L) Fe₃C + Di = Fe₇C₃
- (Fe₇C₃) Fe₃C = L + Di



B: Invariant I3

- (Fe₃C) Fe + Fe₇C₃ = L
- (Fe) Fe₃C = Fe₇C₃ + L
- (L) Fe₃C = Fe + Fe₇C₃
- (Fe₇C₃) Fe + Fe₃C = L

871

872

Table 1: Experimental run conditions

Run	Location	Pressure (GPa)	Temperature (K)
Fe₃C			
RD3 ^a	LDEO	2 ± 0.1	1536 ± 15
07E	Bristol	3 ± 1.1	1766 ± 69
MA1 ^a	LDEO	5 ± 0.5	1798 ± 25
MA2 ^a	LDEO	6 ± 0.5	1878 ± 50
22A	Bristol	7 ± 1.0	1912 ± 75
14B	Bristol	9 ± 1.0	2052 ± 65
21E	Bristol	9 ± 1.0	2223 ± 65
XRD03	ALS	10 ± 1.0	2014 ± 67
XRD04	ALS	10 ± 1.0	1976 ± 69
07C	Bristol	12 ± 1.5	2243 ± 54
14D	Bristol	16 ± 1.0	2244 ± 47
14E	Bristol	16 ± 1.0	2204 ± 68
07G	Bristol	18 ± 1.0	2352 ± 73
07D	Bristol	21 ± 1.8	2381 ± 71
06A	Bristol	25 ± 4.0	2399 ± 68
23A	Bristol	30 ± 1.3	2374 ± 62
XRD06A	Bristol	33 ± 1.0	2459 ± 87
04B	Bristol	34 ± 1.0	2481 ± 94
04C	Bristol	34 ± 1.0	2453 ± 60
01	Bristol	40 ± 2.0	2498 ± 122
05	Bristol	43 ± 2.0	2612 ± 56
10A	Bristol	43 ± 4.0	2658 ± 98
06B	Bristol	44 ± 2.0	2582 ± 121
12C	Bristol	49 ± 2.0	2640 ± 112
12B	Bristol	60 ± 2.0	2824 ± 53
03	Bristol	70 ± 2.0	2971 ± 103
Fe₇C₃			
03B	Bristol	13 ± 1.0	2388 ± 75
03C	Bristol	13 ± 1.0	2375 ± 93
09D	Bristol	20 ± 1.0	2707 ± 53
09E	Bristol	21 ± 1.0	2719 ± 69
04C	Bristol	31 ± 1.0	3004 ± 73
08D	Bristol	34 ± 1.0	2997 ± 69
08E	Bristol	34 ± 1.0	3000 ± 88
12C	Bristol	49 ± 2.0	3122 ± 72
12D	Bristol	52 ± 2.0	3242 ± 82
Fe-Fe₃C			
05B	Bristol	15 ± 3.6	1770 ± 52
36B	ALS	23 ± 1.0	1916 ± 73
37A	ALS	19 ± 1.0	1881 ± 76
03A	Bristol	23 ± 1.0	1963 ± 56
39A	ALS	26 ± 1.0	2042 ± 99
03B	Bristol	32 ± 1.0	2159 ± 67
02	Bristol	37 ± 1.0	2143 ± 50
01	Bristol	42 ± 2.0	2281 ± 74
04A	Bristol	56 ± 2.0	2538 ± 74
04B	Bristol	70 ± 2.0	2627 ± 79

^aData points RD3 (piston cylinder), MA1 and MA2 (multi-anvil) each represent the center point of a bracket, and are not single experiments. See section 3.1 of the main text for details.